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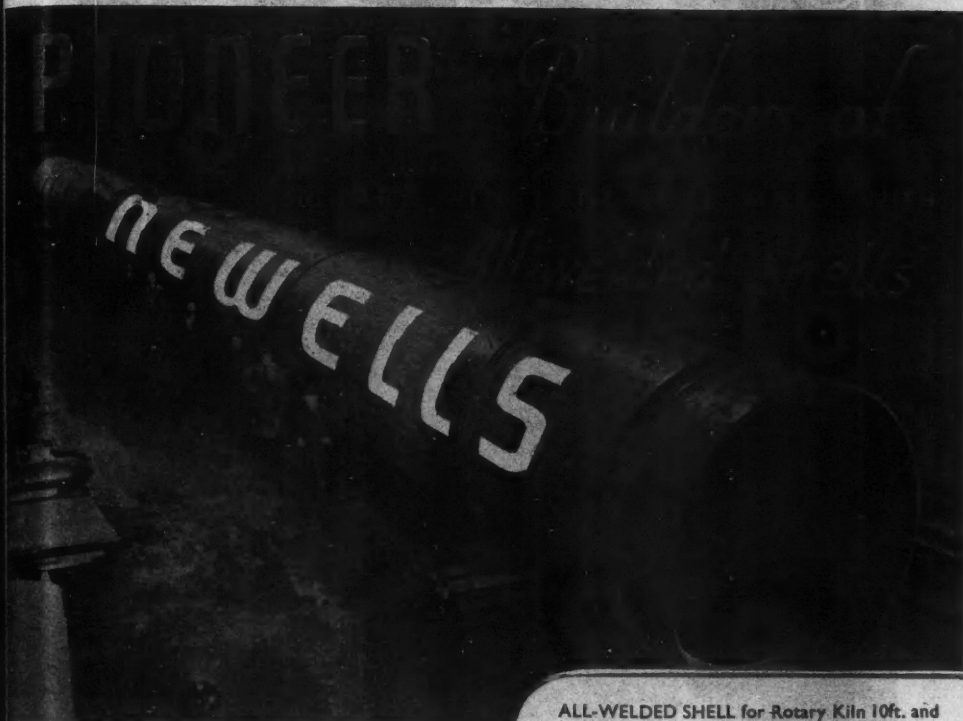
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VOLUME XXI. NUMBER 1

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Hydraulic Hardening of Portland Cement.

By PROFESSOR DR. HANS KÜHL.

SINCE 1893, when W. Michaelis first published¹ his views on the hydraulic hardening of Portland cement as a colloid-chemical process and thereby opposed the opinions of H. Le Châtelier², who six years previously had attempted to account for hardening by a crystallisation process, more than fifty years have elapsed, and it is interesting to examine the history of these two views and the present-day views of the process of hydraulic hardening.

Le Châtelier assumed that the minerals in Portland cement clinker, which he was the first to recognise and describe, first pass into solution, become hydrated, and finally crystallise out as difficultly soluble hydrates, forming acicular crystals which become intertwined and interwoven and thereby adhere together. Michaelis, too, knew that in the hardening of hydraulic binders crystalline structures occur, but he did not attribute any decisive importance to them; indeed he later developed a theory³ according to which the reason for hardening is not to be sought in the formation and interweaving of crystals, but in the production of a colloid gel compound whereby consolidation results from shrinkage, which is itself due to the progressive hydration of the still undecomposed remains of the hydrating cement withdrawing from the gel compound the volume of water required for hydration, a process which Michaelis termed "internal extraction."

The views of Le Châtelier and Michaelis were held by contemporaries to be fundamentally opposed to each other, and it remained for a subsequent age to show that the discrepancy between their views is not after all as great as would appear at first sight. "Crystalline" in Le Châtelier's sense and "colloid" in Michaelis's sense are only contrasts because, when these theories were produced, the distinction between the terms colloid and amorphous was not appreciated. To Michaelis and his contemporaries colloids were amorphous, and the gulf between him and Le Châtelier was unbridgeable. Nowadays, however, the word

colloid merely denotes a state of division, leaving open the question of the composition of the dispersed phase. The dispersed phase of a colloidal system can therefore quite well be crystalline, and it indeed appears as if this also applies to the hydrates of calcium silicate which are produced in the hydration of cements in colloidal gel-producing form. This in any case was the opinion of most of those who met in Stockholm in 1938 to discuss cement chemistry. In what follows extensive use is made of the discussions at the Stockholm symposium, particularly to the papers of G. E. Bessey⁴ on calcium aluminate and calcium silicate hydrates and of S. Giertz-Hedström⁵ on the physical structure of hardened cements.

The difference of opinion between Le Châtelier and Michaelis was not confined to the difference between crystalline and colloidal (amorphous), but extended to the chemical composition of the products of hydration, to the methods of their production, and to the forces which bring about the consolidation of the reacting system of a hardening mass of mortar. All three questions are still of great interest. With regard to the composition of the new formations produced, the difference between the theories of Le Châtelier and Michaelis resided mainly in the silicate hydrates. Le Châtelier believed that the silicates, which are rich in lime, are broken down by the combination with water to form monocalcium silicate hydrate, while Michaelis, for the silicate-gel compounds described by him, expressly refrained from giving a fixed stoichiometric ratio between the lime and the silicic acid although, according to his investigations, it is on the whole possible to assume a molecular ratio of an average of 3 molecules of lime to 2 molecules of silicic acid.

If we ask what is known to-day about the hydrated calcium silicate produced by the hydration of hydraulic binding agents, we must start from the calcium silicates contained in the untransformed binding agents. In Portland cement, silicic acid forms with lime the clinker materials known as Alite and Belite, the first of which contains chiefly tricalcium silicate and the latter dicalcium silicate. In argillaceous cements we are also concerned with dicalcium silicate, yet in many cases the mineral gehlenite $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ can take its place. In blastfurnace slag, the hydraulically active part of which consists of a solidified vitreous mass, the silicic acid is to be sought in this vitreous mass, although it is not possible to make any definite statement about its state of combination.

Some data on the composition of hydrated calcium silicates are furnished by the numerous minerals which occur in the natural state, including okenite, gyrolite, xonotlite, afwillite, and Hillebrandite. Due to their composition, however, it has so far been impossible to obtain any definite information about the hydrated silicates produced by the hydration of the binding agents; this is evidently due to the fact that they are produced under different conditions from those prevailing in the earth's crust. It has been possible to simulate most of the hydrated silicates occurring in nature by artificial means, and frequent use has had to be made of hydrothermal synthesis in the autoclave. The results have not contributed much to the explanation of the hardening problem, no doubt, again, because treatment in the autoclave is different from the hydration process in nature, because at temperatures over 180 deg. C. lime and silicates rich in

lime react with silicic acid, even when it is in the form of quartz which is not very liable to attack. Processes in an autoclave can therefore take place which probably do not occur in nature or in any case is of extreme slowness.

To account for the hydration processes of binding agents it is above all necessary to consider the investigations in which hydrated calcium silicates were produced at low temperatures, whether by causing lime and silicic acid to react directly, or by attempting to make the desired compounds by the double decomposition of calcium salts and soluble silicates, or again by subjecting anhydrous calcium silicates to a hydration process. By different processes it has been possible to make hydrated calcium silicates with four different molecular ratios between the lime and the silicic acid, which can be stated briefly as follows.

(1) Hydrated tricalcium silicate [$3\text{CaO} \cdot \text{SiO}_2 \cdot (1\frac{1}{2}-2) \text{H}_2\text{O}$] was obtained in the form of fine prismatic needles. The production of this compound in the mortar bed of cements rich in lime does not arise here, for reasons that will be discussed later.

(2) Hydrated dicalcium silicate ($2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$) exists in two or even three different modifications, the first of which forms prismatic lattices, the second needles in fibrous or stellar pattern, and the third (if it exists) irregular granules. The forms of the first and second types can be clearly distinguished by their optical properties.³ Tricalcium disilicate hydrate [$3\text{CaO} \cdot 2\text{SiO}_2 \cdot (1-3) \text{H}_2\text{O}$] likewise forms fine needles; the compound has a tendency to gel formation and is difficult to obtain in well defined crystals. A second form with eight molecules of water is said to have been obtained by S. Nagai⁶ with hydrothermal synthesis⁴. Monocalcium silicate hydrate [$\text{CaO} \cdot \text{SiO}_2 \cdot (0.2-0.5) \text{H}_2\text{O}$]. This compound, which also crystallises in fine needles, does not come under consideration as a product of hydraulic hardening, just as was the case with tricalcium silicate hydrate.

In order to be able to judge with certainty which of the possible hydrated calcium silicates are actually produced in hydraulic hardening, it is necessary to have some knowledge of the equilibria between them and their aqueous solutions. Unfortunately the references in literature to this question are often contradictory. According to G. E. Bessey⁴ the most reliable information is contained in a paper by E. P. Flint and L. S. Wells.⁷ These writers caused colloid solutions of silicic acid and lime water to react with one another at 30 deg. C. and obtained the ratios between the composition of the precipitates produced (hydrated calcium silicates) and the concentrations of lime and silicic acid in the solutions in equilibrium with the precipitates. The results gave rise to the solution diagram (Fig. 1), in which there can be read off by means of the solubility curve ABCDE on the abscissa of the system of co-ordinates the amounts of lime and on the ordinate the amount of alumina (argillaceous earth) in the solution. The composition of the precipitates corresponding to each point on this curve may be taken from the corresponding points on the straight line MN, expressed by the molecular ratio $\text{CaO} : \text{SiO}_2$ in the precipitate. The diagram shows that the ratios in the range of the silicates poor in lime are rather complicated, since silicic acid concentrations of greatly varying proportions may be assigned to a lime concentration of 0.05 to 0.1 gramme CaO per litre. This matter will not, however, be pursued further, because hydrated calcium silicate with less than one molecule of lime per molecule of silicic acid does not come under consideration ;

we are only concerned with that part of the curve which, starting at point D, proceeds to the right. At point D hydrated monocalcium silicate and silicic acid are in equilibrium with each other and with a solution which contains about 0.05 gramme of lime and 0.04 gramme silicic acid per litre. If the lime content of the solution continues to rise the quantity of silicic acid in solution will decrease very rapidly, so that even with a lime concentration of 0.12 gramme of CaO per litre quantities of silicic acid of 10 to 15 mg. only are found, and with lime

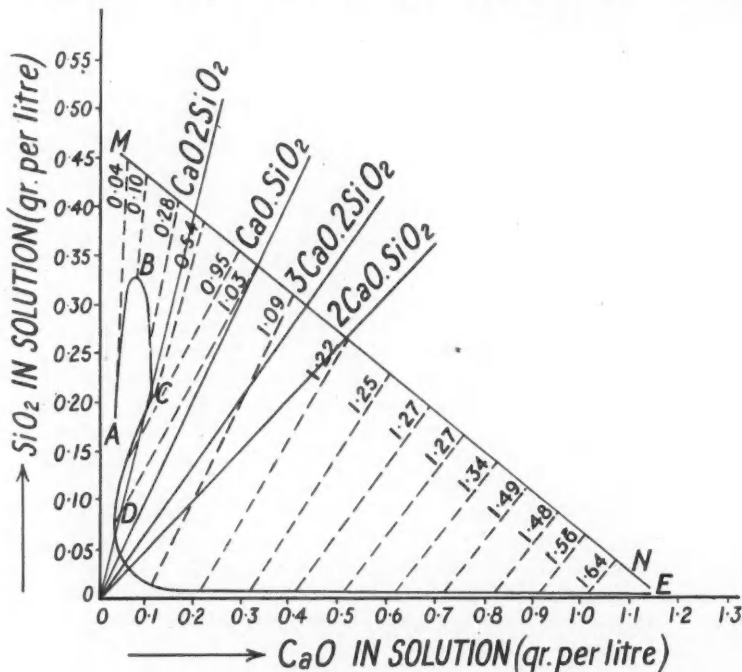


Fig. 1—Solubility Ratios of Hydrated Calcium Silicate at 30 Deg. C.

concentrations which exceed 0.2 gramme per litre the solubility of the silicic acid drops to 1 to 2 mg. The extraordinary low solubility of silicic acid in lime water in fairly large concentrations makes it impossible to specify points on the curve where, for example, hydrated tricalcium silicate would be in equilibrium with monocalcium silicate hydrate or dicalcium silicate hydrate. Nevertheless, on the position of these equilibria depends which hydrated calcium silicate is produced in the hydration of binding agents that are rich in lime, the chief point to be decided being whether we are concerned with the hydrated silicate with the molar ratio 3:2 or that with the molar ratio 2:1, since the original view of Le Châtelier, that the silicates rich in lime in the binding agent are broken down to form hydrated monocalcium silicate, has had to be abandoned.

Although Flint and Wells's curve does not show where the equilibrium lies

between the 3 : 2 and the 2 : 1 silicate, investigations by G. E. Bessey have made it highly probable that a gel with the molar ratio of about 3 : 2 is in equilibrium at 17 deg. C. with a solution containing 1.1 gr. of CaO per litre, that is a solution which is not far removed from the concentration of saturated lime water. With a still higher lime concentration up to the point of saturation, the composition of the precipitate approaches the molar ratio of 2 : 1, from which may be drawn the important conclusion that the hydrated dicalcium silicate can only exist in contact with a lime-water which is very close to saturation; when the lime concentration is only slightly less its place is taken by hydrated tricalcium silicate.

If the hydration of the hydraulic binding agents always concerned saturated or unsaturated lime-water, it would follow that in the course of hydration the compound $2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ must be formed. The very fact that these equilibria data relate to normal temperatures, while in the hydration of binding agents considerable increases in temperature occur and the solubility of the lime drops as the temperature rises, makes it possible that this increase in temperature is in itself sufficient to render the formation of dicalcium silicate hydrate impossible, producing instead the hydrate with the molar ratio of 3 : 2. There is, in addition, the fact that in the hydration of binding agents calcium salts such as calcium sulphate and aluminate, as well as lime, pass into solution, and that most binding agents also contain alkalis, which in turn pass rapidly and in considerable quantities into the fluid phase. All these factors must reduce the concentration of the calcium hydroxides in the liquid phase and thereby contribute to shifting the equilibrium from the hydrated dicalcium silicate to the hydrated tricalcium silicate. Although many still hold the view that in the hydration of Portland cement the compound $2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ is produced, it seems that there is a greater likelihood of the formation of hydrated tricalcium disilicate. I therefore share the outlook of those who consider that the decomposition of the tricalcium and dicalcium silicate forms hydrated tricalcium disilicate, and base my views both on the older investigations of Michaelis and on the results reached, among others, by G. E. Bessey,⁴ T. Thorvaldson and V. A. Vigfusson⁸, P. Schläpfer⁹, and myself with my collaborators T. Wang¹⁰ and A. Mann¹¹.

While we are acquainted with many natural hydrated calcium silicates, only a single hydrated calcium aluminate is known in the natural state; this is known as hydrocalumite, and its composition is $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$. The composition of this mineral shows that, in contrast to silicic acid, argillaceous earth (alumina) has the power of forming hydrated aluminates which are rich in lime. The number of artificially-produced hydrated calcium aluminates is, allowing for all the modifications, a large one. According to the lime content, however, this number is reduced to five compounds, corresponding to a content of 1, 2, 3, 4, and 5 molecules of lime to one molecule of silicic acid. The hydrates which are richest and poorest in lime have not so far been significant in explaining the hydration processes in hydraulic hardening, but on the other hand the aluminates with 2, 3, and 4 molecules of lime are important. These compounds may be briefly summed up as follows: (1) Hydrated tetracalcium aluminate [$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot (12-13)\text{H}_2\text{O}$] exists in two or perhaps three different modifications; they all

form hexagonal or pseudo-hexagonal forms, which exhibit only slight differences in their optical properties. Compared with natural hydrocalumite there are also certain differences, which are probably due to the fact that the natural mineral always contains some carbonic acid. (2) Hydrated tricalcium aluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$) exists in three modifications, which are characterised by a very different content of water of crystallisation. The most highly-hydrated compound with eighteen H_2O crystallises in long biaxial needles. Particularly characteristic as the only hydrated calcium aluminate crystallising in the regular system is the lowest hydrated compound with six molecules of water; it crystallises according to the lime concentration of the solution from which it separates out, in cubes, octahedrons, dodecahedrons, and icositetrahedrons. Between these two compounds there is a hydrate which crystallises with 11 to 12 molecules of water and forms hexagonal plates. It would seem that at temperatures up to about 30 deg. C. the compound with $12\text{H}_2\text{O}$ is stable, and at higher temperatures the regular compound with $6\text{H}_2\text{O}$ is stable. (3) Hydrated dicalcium aluminate [$2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot (7-9)\text{H}_2\text{O}$] crystallises in hexagonal plates, which often merge to form spherolytic clusters.

The equilibrium conditions between the different hydrated aluminates and their aqueous solutions are highly complex. It is particularly difficult to gain an insight into them because the equilibria adjust themselves extremely slowly, and months of observation are frequently required before an equilibrium is established between two hydrates. A further difficulty is that the separation of the hydrated aluminates from their solutions by no means always follows the phase rule, and that, as G. Assarsson¹³ in particular has shown, effects of concentration and temperature are of far greater importance than the equilibrium ratios between the hydrates.

Some guidance with regard to the reciprocal ratios between the different hydrated aluminates, which are of importance for the hydraulic hardening process, is provided by a diagram by G. E. Bessey⁴ (Fig. 2). To read from the diagram the equilibrium conditions of the hydrated aluminates with 2, 3, and 4 molecules of lime, which are important for hydraulic hardening, first consider the point marked A, which corresponds to the congruent solubility of hydrated tricalcium aluminate with six molecules of water, so that when equilibrium is established the solution contains 0.17 gramme of lime and 0.11 gramme of alumina per litre. The section of curve OA represents the solubility curve of the aluminium hydroxide as a function of the lime concentration, so that at point A aluminium hydroxide and hydrated tricalcium aluminate are in equilibrium with each other and with the solution. With a further increase in the lime content, the alumina content drops sharply and the curve resembles that for the calcium silicates. It has nevertheless been possible to establish that at point B, with a concentration of 1.07 gramme of lime and 0.003 gramme of alumina per litre, there is an invariant equilibrium, namely the equilibrium between hydrated tetracalcium aluminate and one of the hydrated tricalcium aluminates. The part of curve BC then probably corresponds to the solubility of the hydrated tetracalcium aluminate, but it may possibly be a question of an extension of the solution curve of the

hydrated tricalcium aluminate. It depends on which of the two compounds may be regarded as stable in this range, and which as metastable, a question which is still awaiting an answer. At point D, where the solution contains 0.36 gramme of lime and 0.33 gramme of alumina per litre, we are probably concerned with the congruent solubility of the hydrated dicalcium aluminate, which would be found here in metastable equilibrium with aluminium hydroxide whose metastable solubility follows the curve AD. In the figure DEB are a few more points to which different research workers have attributed special importance

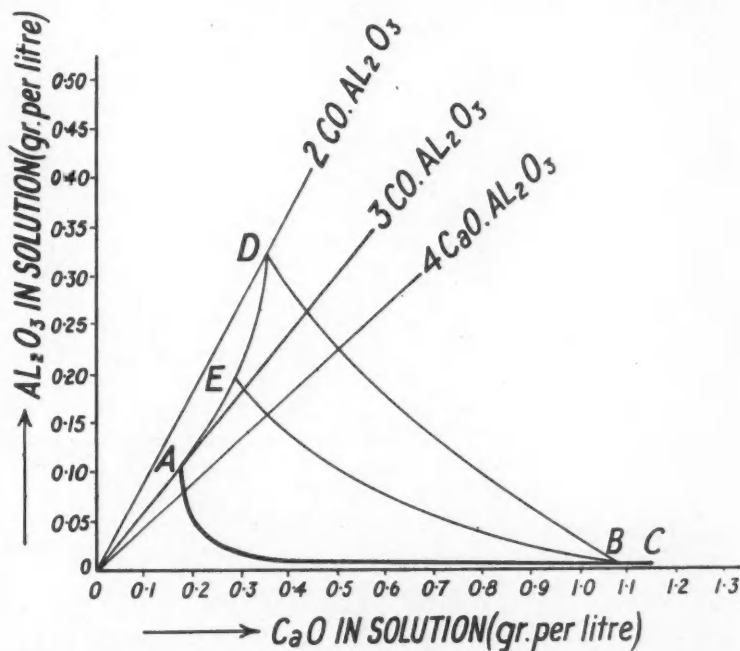


Fig. 2.—Solubility Ratios of Hydrated Calcium Aluminate at 25 degs. C.

as points of invariance between different hydrates; nevertheless, the actual conditions are so uncertain that it is useless to go into details.

Owing to the uncertainty which exists on some points with regard to the hydrated silicates and aluminates, it is not yet possible to state definitely which hydrates occur in the hydration processes of the different hydraulic binding agents. In a very summary fashion, however, it is possible to assume that in the hydration of the cements rich in lime, for example, Portland cement, hydrated tetracalcium aluminate is mainly formed, and in the hydration of cements poor in lime, for example, high-alumina cements, hydrated dicalcium aluminate is mainly formed. In both cases, however, it is possible that hydrated tricalcium

aluminate is also formed, and certain phenomena associated with the dependence on temperature of the hardening curve of high-alumina cements make, according to F. M. Lea¹³, the presence of this compound highly probable even in systems that are poor in lime.

The third important constituent of hydraulic binding agents which should be considered are the ferrites, either the tetracalcium aluminate ferrite in Portland cement or one of the ferrites free from alumina in high-alumina cements. During the hydration of ferrite compounds, hydrated calcium ferrite is undoubtedly formed, and investigations so far available show that between the hydrated aluminates and the hydrated ferrites there is a certain parallelism inasmuch as the different hydrated ferrites correspond to hydrated aluminates with the same molecular ratios. In particular the following has been found. (1) Hydrated tetracalcium ferrite ($4\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 14\text{H}_2\text{O}$), according to H. Hoffman¹⁴ in constant contact with lime-water containing at least 1.06 grammes of CaO per litre; (2) Hydrated tricalcium ferrite ($3\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$), according to A. Eiger¹⁵ corresponds to the hydrated tricalcium aluminate with six molecules of water; in its properties it exhibits a far-reaching analogy with that compound. Its limit of stability is a solution with 0.25 gramme of CaO per litre. (3) Hydrated dicalcium ferrite ($2\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$) was obtained by R. H. Bogue and Wm. Lerch¹⁶ as an amorphous gel during the hydration of dicalcium ferrite.

Further details regarding the conditions of equilibrium cannot be specified because the published observations are contradictory. According to Hoffmann, in addition to the hydrated tetracalcium ferrite there is a hydrate with a lower lime content which is stable in contact with lime-water having 1.06 to 0.64 grammes of CaO per litre, while below 0.64 gramme of CaO per litre complete hydrolysis occurs. The observations of E. Eiger concerning the limits of stability of the hydrated tricalcium ferrite do not agree with those of Bogue and Lerch; these observations are, however, sufficient to justify, with a fair degree of accuracy, the assumption that the hydrates produced during the hydration of ferrites are entirely analogous to the hydrated aluminates; in cements rich in lime, hydrated tetracalcium and tricalcium ferrite can be considered and, in cements poor in lime, hydrated dicalcium and tricalcium ferrite. It has long been assumed that the compounds which can be formed during the hydration of cements as hydrates are limited to silicates, aluminates, and ferrites. Investigations by W. Strätling¹⁷, however, make it appear possible that we must also reckon a quaternary compound as the product of hydraulic hardening—with a hydrated calcium aluminate silicate which would correspond to $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$. This compound, which is analogous to gehlenite, could not be obtained directly by the addition of water to gehlenite, yet it was formed together with hydrated tricalcium silicate as a result of the action of lime-water on dehydrated kaolin, and also in a reaction of tricalcium silicate and tricalcium aluminate with water.

Among the secondary constituents of cement some free lime is present, and there are always alkalis. Moreover, many phenomena associated with the setting process are greatly, and often very greatly, influenced by these constituents; nevertheless, these compounds have in the past had little importance

attached to them in the theory of hydraulic hardening, so some reference must be made to the reactions which they undergo during hydration. The same applies to the formation of certain double salts with the participation of the hydrated tricalcium aluminate, the most important of which is hydrated tricalcium aluminate sulphate of the formula $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot (30-33)\text{H}_2\text{O}$. This compound comes about through the reaction between hydrated tricalcium aluminate and calcium sulphate, and it therefore forms an integral part of the hardening products of gypsum-containing Portland cements. Its significance does not, however, reside in this fact, but in the phenomenon of the expansion of gypsum which can be brought about by a particularly large formation of this double salt, as is recognised by E. Candlot (¹⁸) and W. Michaelis (¹⁹). Owing to this harmful property, and to the occurrence of this compound in the form of fine needles, Michaelis termed it "cement bacillus."

What conclusions can now be drawn from our knowledge of the existence and the conditions of stability of the hydrated compounds which come about in the setting and hardening processes of hydraulic binding agents?

If we consider first cements with a high lime content, that is, Portland cement with or without admixtures of blastfurnace slag, the liquid phase throughout all the stages of hardening exhibit a light lime concentration, and consequently the production must be reckoned with those formations which correspond to such a lime concentration. It must therefore be assumed that hydrates are produced from the aluminates and ferrites of the binding agent; these hydrates contain four or at least three molecules of lime to one molecule of acid components, and are therefore richer in lime than the original compounds from which they were formed. Conversely, during the hydration of the calcium silicates there must be a disintegration in the lime, which very likely advances to a molar ratio of 3:2 and in which, therefore, dicalcium silicate takes part with tricalcium silicate.

As the proportion of silicate components in cements far exceeds that of the other constituents, of the quantity of calcium hydroxides split off during the hydration of the silicates only a small part is used in order to form the unhydrated aluminates and ferrites into their hydrates, which are rather richer in lime. The bulk of the calcium hydroxide therefore remains free, and in consequence free hydrate of lime forms an important constituent of the hardened hydraulic binding agent, which is rich in lime; it forms relatively large crystals, which are to be found in hardened cement fairly easily under the microscope in the form of hexagonal plates.

The aluminates again form on hydration microscopically discernible, although smaller, crystalline structures, but it is to be assumed that—at least in the early stages of hardening—the hydrated aluminates produced are so finely divided that the dimensions of the crystals approach colloidal dimensions. The same should apply to the ferrite setting products, and also to the hydrated calcium aluminosulphate.

Although new crystalline formations are produced in large quantities during hydration, the hydrated calcium silicate, as the only colloidal product of hydration,

preponderates quantitatively and, of the new products derived from the hydration process, is mainly responsible for determining the hardening process.

The position is quite different in the case of a cement poor in lime, for example, high-alumina cements. The fact that the silicic acid in the alumina cements never combines with more than two molecules of lime, shows that there can be no question of the release of large amounts of lime in the hydration of alumina cements. On the other hand, alumina has a tendency to form hydration products rich in lime, and since in high-alumina cement there is generally less than one molecule of lime to one molecule of alumina, the production of alumina hydrates rich in lime, even allowing for the fact that from the hydration of the dicalcium silicate a little lime is released, is only possible by part of the alumina yielding up its lime in order to enable another portion to form hydrated dicalcium or tricalcium aluminate. The alumina released in the hydration process plays in the hardening of high-alumina cements the same part as hydrated calcium silicate in that of cements rich in lime: the alumina is separated as colloidal aluminium hydroxide and, just as in Portland cement colloidal calcium silicate is the operative factor, so in high-alumina cement colloidal aluminium hydroxide is the real and essential factor in hardening and imparts its typical properties to the cement when set.

Although we have obtained some insight into the products of hydraulic hardening, nothing has yet been said of the way in which these substances are formed. As already mentioned, Le Châtelier assumed that all the components of the cement which are capable of hydration first pass into solution, become hydrated in the solution, and are then separated again from the solution as difficultly-soluble hydrates. This is the view which I have held in the past ²⁰ and is still held to-day by a number of research workers, including G. E. Bessey⁴ and L. Forsén²¹.

Michaelis held a different view of the hydration of silicates rich in lime. He believed that from these compounds, without their passing into solution, part of their lime is extracted by the water and a porous residue remains which then, under the influence of the lime-water which is produced, swells to form the gel mass of the hydrated calcium silicate. This conception was scarcely compatible with the older views of physical chemistry, for it was assumed that a chemical compound either passes into solution as a whole or remains undissolved, but that the release of certain components from a molecular combination was impossible. It is true that even in those days the phenomenon of base exchange and release of water in the case of zeolites provided food for thought, but it remained for our knowledge of lattice structure and the interchangeability of lattice components to show that conceptions such as those of Michaelis should not be rejected on principle.

Since all the components of hydraulic binders are slightly—generally very slightly—soluble in water, there can be no divergence of opinion that all new formations can come about by the components of the cement passing into solution, becoming hydrated, and separating out again. The only question is whether this process takes effect for all the components by itself, or whether there

is not direct hydration somewhat on the lines of Michaelis. Attempts have been made to answer this question by theoretical considerations and by practical experiments. Reference should be made to the statements by L. Jesser²². In his reflections on the forces which bring about the consolidation of cement mortar, Jesser comes to the conclusion that the reaction between the components of the binder and the water does produce new chemical compounds, but that the particle volume of the original material is retained and the individual cement granule continues its existence in the hardened mortar. On this assumption it would have to be supposed, for all new formations derived from hydration, that they are not separated out from a solution, but that they come about through the direct addition of water to the anhydrous compounds. In tests on the reaction course of the hydration process of Portland cement clinker and clinker grit, the writer and T. Wang²³ came to the conclusion that the aluminate components of cement first pass into solution and separate out of solution as hydrates, but that the silicate components react very differently inasmuch as they cause about half their lime to pass into solution relatively violently, but then become hydrated in the cement granule and thus form a calcium hydrosilicate which surrounds the cement granule as a gel. On a superficial observation it may seem rather immaterial whether the hydration products are formed in one way or another. For an understanding of the hardening process and its concomitant phenomena this question is, however, of paramount importance, for if the new growths separate out from the liquid phase this separation will take place for preference at the points of least resistance, namely, in any pore spaces present, whereas in the case of a hydration process associated with a definite point the new formations must accumulate at that point, whereby forces are released at that point which otherwise—in the case of separation from the liquid phase—do not exist. This question is not so much of importance for the normal hardening process as for explaining the expansion that can occur in the case of badly-made specimens or concrete or as the result of chemical attack. This reference must, however, be sufficient, for the problem of expansion does not come within the scope of this article.

Now that we have seen which new formations emerge from the hydration process and the manner in which they come about, the third and last question arises: How is it that the hydration processes entail such a degree of consolidation of the reacting system that out of a doughy mass a hard stone of great strength is finally produced? Le Châtelier believed that he could account for it by assuming that the crystal needles become matted, much as in the process of the hardening of gypsum, while Michaelis assumed that a gel mass is constantly deprived of water and thereby becomes increasingly more solid. Michaelis probably did not follow up the question of why a high degree of strength is attained by this deprivation of water. The writer does not think that Michaelis had thought of the views of later research workers, who have understood the theory of "internal extraction" to mean that the particles of hardened cement are held together by certain suction forces derived from the removal of water. Michaelis took for granted the consolidation of a gel subjected to dehydration, and by the term "extraction" merely

denoted the transfer of water from the hydrated gel to the not yet hydrated core of the cement granule. The word "extraction" should therefore be equated with the word "transfer," without thereby implying the effect of forces.

We come to the modern conceptions of the forces which combine the particles of set cement to form a mass with the hardness of stone if we follow the reasoning of S. Giertz-Hedström⁵, who bases his considerations on the following four basic premises. (1) A cement mortar slaked with water consists by volume, as a rough approximation, of about 1 part cement and 2 parts water (if for the cement we assume a specific gravity of 3.1, such a cement mortar has the water-cement ratio of 0.65). (2) In the hydration process about half the water is chemically combined by the cement and thereby transferred from the liquid to the solid state. In this way the ratio—again calculated in parts by volume—of the solid to the liquid phase is changed from the numerical ratio 1:2 to the numerical ratio 2:1. (3) Hydration entails a reduction in the total volume of the liquid and solid phase; it is therefore accompanied by a contraction which can only to a limited extent give rise to the hardening system, so that pore spaces must occur in the hardening cement. (4) The reactions brought about by the combination of water, owing to the colloidal nature of the hydrated calcium silicate being formed, entail a considerable increase in the internal surface of the system, so that the reduced fluid portion is now distributed over a very much larger surface of the solid phase with the result that the liquid can only be present in the form of thin films between the new formations. The transition of the mortar from the condition of "water abundance" in (1) to the "water poverty" condition in (2) constitutes the actual cause of consolidation, for this transition paves the way for the effectiveness of the capillary and boundary surface forces which are the result of the changes in the hardening system as in (3) and (4).

The production of the pore spaces as a consequence of the hydration reaction must—as K. Wurzner²⁴ has repeatedly pointed out—release capillary forces which bring about a suction effect within the reacting system as a result of which the mass of mortar is consolidated. Nevertheless, the actual strength of the cement depends not so much on the action of these capillary forces as on the effect of forces of adsorption and cohesion, which become effective on the boundary surfaces of the particles of the fine colloidal gel structure.

While Giertz-Hedström is of the opinion that in the final condition the particles of the gel mass are held together by effective adhesive forces between them, T. Maeda²⁵ concludes from the investigations of himself and his collaborator S. Yamane with Sorel and Portland cements, that the real vehicle of the strength properties in hardening cement is to be sought in the films of water which connect the gel particles with one another. Maeda states that the reduction in the proportion of the liquid phase and the enormous increase of the inner surface of the solid phase must result in the thickness of the film of water between the particles of the fine gel structure decreasing to almost molecular dimensions. Thus the properties of the liquid water alter so that it passes into a pseudo-solid condition, and in the end it would be this pseudo-solid water that determines the strength of the hardened cement. Similar conclusions have been arrived at by L. Jesser²², although from

a different direction. Jesser has evolved a theory of hydraulic hardening which goes into details; he starts from the active electrostatic boundary surface forces in colloidal systems. Jesser's theory is not a simple one, but it would seem that his considerations are likely to lend further support to our conception of the essence of hydraulic hardening as a colloidochemical process. Although Jesser is compelled to make certain theoretical assumptions regarding which there may be some difference of opinion, he has nevertheless made use of the entire range of modern colloidal chemistry, and by its aid sketched a picture of the colloidal hardening process which is a considerable improvement on the conceptions which the creator of the colloidal hardening theory, W. Michaelis, took as his basis. A noteworthy feature of Jesser's views is that the pre-requisite for the production of the colloidal gel mass is furnished before hydration in the structure of the calcium silicates of the cement, and therefore it is not the chemical reactions to which the calcium silicates are subjected that are the important factor, but rather the electro-kinetic processes in the mortar compound and the electrostatic forces resulting from them in the boundary surface area between the solid and the liquid phase. On the basis of these ideas Jesser concludes that in the hydration of the silicates at least topochemical reactions are concerned, that is to say processes which take place on the surface of the cement granule, without a solution process and confined locally. Owing to these topochemical processes, the cement granule is subjected to a permanent chemical change without, however, entirely disappearing, and on the strength of this opinion Jesser was able to formulate the thesis that the unhydrated cement particle is conserved as an individual even in hardened cement.

If from the conception of hydraulic hardening as a colloidochemical process we reach the view that in the ultimate resort hardening depends on the reduction of the liquid phase and its gradual transition into the solid and pseudo-solid states, it is not without interest to endeavour to ascertain the form in which water is finally contained in the hardened cement. According to the theories mentioned, at least four different stages of water combination can be distinguished. The most rigidly combined water occurs in the molecular combination of the hydrated silicates, aluminates, and ferrites produced in the hydration process; here it forms an integral part of these compounds and can be termed "solidified." Somewhat less rigidly combined is the water which surrounds the gel particles as the adsorption layer and which, in the opinion of Maeda and Jesser, as a pseudo-solid film brings about the cementing of the fine structural particles of the gel. Thirdly we have the water drawn into the fine capillaries of the hardening cement; this water can no longer be regarded as actually combined or even as pseudo-solid, but it is altered by the capillary forces which retain it in that its vapour pressure is lessened, and it is consequently difficult to eliminate from the cement mortar by raising the temperature or by extraction. Finally there is the water imbibed by the larger pores and cavities of the cement. This water can still be termed "free water," although it contains a number of constituents of cement in solution, especially alkalis, and also small quantities of alumina and silicic acid. Nevertheless, the concentration of these dissolved constituents is not so

great as to change appreciably the vapour pressure of the water and its behaviour in respect of the laws of osmotic pressure.

If as against these four clearly different stages of water formation Giertz-Hedström distinguishes a fifth stage, in which he includes "the water utilised by dissolved and solvatised substances and retained to some extent by them," the writer cannot altogether share his view, for it will scarcely be possible to set a limit between this and the water termed "free."

As the result of observations in connection with the hardening process, the set cement seems to the writer to be a shrunken gel mass of a hydrated calcium silicate, traversed by fine pores and channels, consisting very probably of three molecules of lime and two molecules of silicic acid, and in which are embedded besides remains of unconsumed original compounds, fine crystalline new formations of hydrate of lime, hydrated calcium aluminates, ferrites, and aluminosulphate. Hardening is partly due to the capillary forces acting in the finely porous system, but is principally attributed to the interplay of the boundary surface forces which are active between the sub-microscopic, possibly amorphous, and very likely micro-crystalline, particles of the gel mass; on a small scale they bring about directly, or through the agency of pseudo-solid films of water, a rigid cohesion of the gel particles, and thus on a large scale produce the stone-like consolidation of the hydraulic binders.

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New Specification for Portland Cement in Czechoslovakia.

A NEW specification for cements, No. CSN-1213, was published in Czechoslovakia in 1947. The requirements for Portland cement differ in some particulars from those in the specification of 1934.

The maximum amount of SO_3 is now 3 per cent. compared with 2.5 per cent. in the 1934 specification, and Mg not more than 6 per cent. compared with 5 per cent. The amount of CaO expressed as a ratio of the amount of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ must not exceed 1.7.

The setting times are unaltered and are, for ordinary Portland cement, not less than one hour for the initial setting and not longer than 15 hours for final setting. For high-strength cement, initial setting must take place in not less than 30 minutes and in not more than one hour; the time of final setting is not more than 15 hours. The requirements regarding fineness are, as in 1934, a residue of not more than 2 per cent. on a sieve having 900 meshes per square centimetre (diameter of wire, 0.1 mm.) and not more than 20 per cent. on a sieve having 4,900 meshes per square centimetre (diameter of wire, 0.05 mm.).

The tensile strengths of briquettes of ordinary cement are 256 lb. per square inch at 7 days and 356 lb. per square inch at 28 days. The corresponding compressive strengths are 2,845 lb. and 3,911 lb. per square inch. The tensile strengths of high-strength cement at 3 days, 7 days, and 28 days are respectively 356 lb., 398 lb., and 427 lb. per square inch, the corresponding compressive strengths being 2,845 lb., 5,334 lb., and 6,045 lb. per square inch.

The compressive tests are made on cubes having an area of face of 50 sq. cm. The shape of the standard briquette differs from that in the British Standard; it is 22.2 mm. thick (that is 0.870 in. compared with 1 in.) and at the waist, which is about 26 mm. wide, there is a reduction to 22.5 mm. (0.886 in. compared with 1 in.).

Lime in Portland Cement.

A FORMULA for determining the limiting amount of lime in Portland cement in the system $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3-\text{MgO}$ has been recently derived in Russia and is given in "Building Science Abstracts." The formula, which has a hypothetical basis is

$$\text{CaO} = 2.8 \text{ SiO}_2 + (\text{Al}_2\text{O}_3 - 0.64 \text{ Fe}_2\text{O}_3) + 1.4 \text{ Fe}_2\text{O}_3.$$

Examination of ten experimental clinkers showed that the limiting amount of lime is $2.8 \text{ SiO}_2 + \text{Al}_2\text{O}_3 + 0.7 \text{ Fe}_2\text{O}_3$ when the Al_2O_3 modulus exceeds 2, and $2.8 \text{ SiO}_2 + 1.65 \text{ Al}_2\text{O}_3 + 0.35 \text{ Fe}_2\text{O}_3$ when the Al_2O_3 modulus is less than 2.

The Supply of Ready-mixed Lime Mortar.

BEFORE the introduction of hydrated lime sold in paper bags, the manufacture of lime-mortar on a building site was an operation requiring manual labour of the hardest kind in beating up the putty after the lime had been slaked. On small works the slaked lime and sand were also mixed by hand. The use of hydrated lime has saved the labour required for slaking lump-lime on the site, and also the space occupied by the lime during the period of three weeks or so required for the maturing process.

On the Continent ready-mixed lime-mortar has been supplied for nearly fifty years. In 1939 the first ready-mixed lime-mortar plant in Britain was started at Ryton-on-Tyne by Lime-Sand Mortar, Ltd., and this company now has works in operation at Knaresborough, Manchester, and Riverhead (Kent). Each of these works has a capacity of 600 tons a day, which can be increased to 1,000 tons a day by duplicating some of the machinery. The following notes



Fig. 1.—General View of Ready-Mixed Mortar Plant.

and the illustrations describe the works at Riverhead, which is similar to the other three plants.

Views of the works at Riverhead are shown in *Figs. 1* and *2*. In *Fig. 1* the building in which the lime putty and sand are mixed is seen in the left foreground, the building in which the lime is slaked is near the middle, and the sand pile is on the right. *Fig. 2* shows the mixing building on the left and the slaking building (nearing completion) on the right, with the tanks for maturing the slaked lime between the two buildings.

Non-hydraulic lump lime is delivered by lorry and tipped into the boot of a continuous bucket-elevator which takes it to a hopper of 30 tons capacity over a pair of pans on the right of *Fig. 2*. The required quantities of lime are discharged into the pans, water is added, and the contents of the pans are kept stirred by rotating arms until the lime is thoroughly slaked (*Fig. 3*). From the slaking pans the lime-milk is conveyed along wooden flumes to any one of a series of brick-built storage tanks with a total capacity of approximately 600 tons (*Fig. 2*), where it is left to mature for three to four weeks. There is a channel containing a screw conveyor between the two rows of maturing tanks. Lime

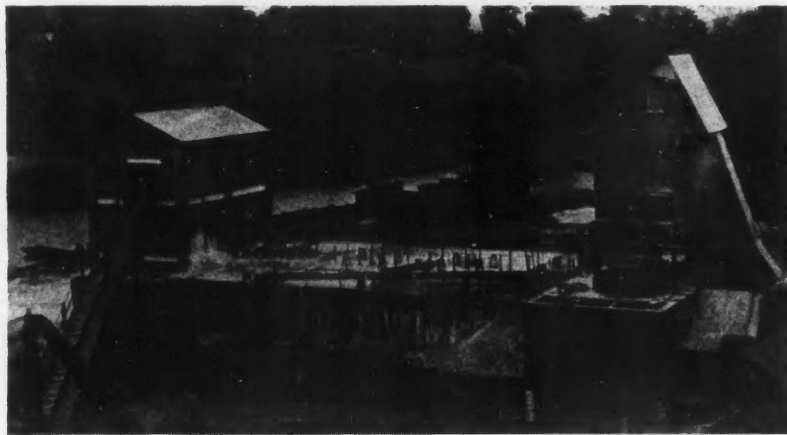


Fig. 2.—Lime Slaking Pans on Right, Maturing Tanks in Middle; Mortar-mixing Building on Left.

putty is discharged from a maturing tank through sluice gates into this channel, the screw conveyor changes the putty to a creamy consistency, and conveys it to a collecting tank on the ground floor of the mixer building (on the left of *Figs. 1 and 2*), and from there it is pumped to a storage tank on the top floor of the building. This storage tank contains enough lime-cream for about 30 tons

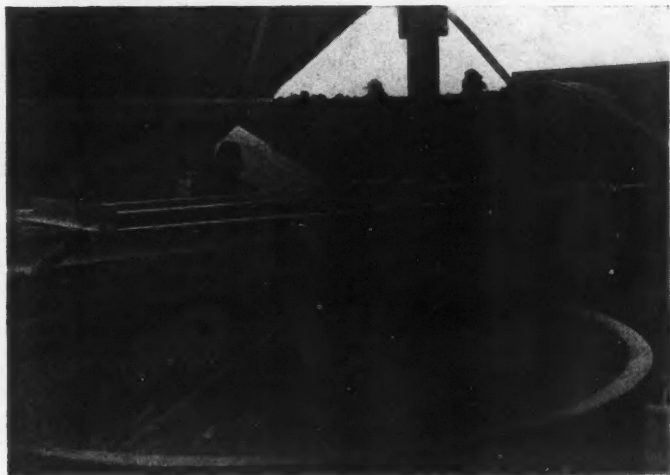


Fig. 3.—Lime-slaking Pan.

of mortar and is equipped with a stirring gear to prevent the lime-cream settling to putty again. A pipe leads from the storage hopper to the mixer situated on the floor below.

About 6,000 cu. yd. of washed sand are stored in a pile so that excess water will drain away from it, and it is picked up by a boom-scraper and taken by means of an inclined belt conveyor to a storage hopper on the top floor of the mixer building. The outlet of the hopper leads to a belt feeding the mixer (*Fig. 4*). The rate of supply of the sand is constant, and the correct proportions



Fig. 4.—Mortar-Mixer.

Sand is delivered by the conveyor on the right; lime-slurry is delivered through a pipe in the foreground; the screw at top of the photograph passes the mortar to the loading chute seen in *Fig. 1*.

of sand and lime are maintained by controlling the quantity of lime by a butterfly valve in the delivery pipe. The mixer is in the form of a screw, which propels the mortar as it is mixed and passes it into a chute from which it falls into a lorry.

It will be seen that the process takes advantage of the old method of using non-hydraulic lime and leaving it for some weeks to mature, but relieves the builder of the task of slaking the lime and mixing it with sand. Also, mortar

made in a factory can be more carefully controlled than on a building site, with the result that the product is generally more uniform, stronger, and more plastic than a mortar made by a builder. The sand used is well graded and clean, and it is not necessary to use a loamy or dirty sand to obtain the necessary degree of plasticity; it is claimed that the high degree of plasticity of ready-mixed mortar enables the bricklayer to lay considerably more bricks in a day. Provided that air is excluded by heaping up the mortar and smoothing its surface with a trowel, the mortar can be kept for a considerable period without losing any of its properties when it is beaten up with water for use. The mortar dries out white, but pigments can be added if a coloured mortar is wanted, and it can be gauged with Portland cement if desired. It is also claimed that ready-mixed mortar is free from efflorescence. The limit of economical distribution by road is thirty miles. Messrs. Hall & Co., Ltd., are the agents for the sale of the product of the Riverhead works.

The Suitability of Blastfurnace Slag for the Manufacture of Cement.

IN an article in "Verre et Silicates Industriels" for March and April, 1947, Mr. A. O. Purdon, B.Sc., A.R.I.C., discusses methods of determining the suitability of blastfurnace slags for the manufacture of metallurgical cements.

The reaction of the slag depends not only on the chemical composition but equally on the conditions of cooling. If a slag cools slowly it crystallises, and in this state it is less reactive. To prevent crystallisation the slag is cooled quickly as it emerges from the blastfurnace and becomes granular in which form it is used in the manufacture of metallurgical cements. The chemical composition is diverse, the three principal constituents being silica (SiO_2), 25 per cent. to 40 per cent.; alumina (Al_2O_3), 10 per cent. to 25 per cent.; and lime (CaO), 35 per cent. to 50 per cent.

The analysis of about thirty slags from Belgium and five from Britain gave the following average and extreme compositions:

	Belgian slags			British slags		
	Average (per cent.)	Minimum (per cent.)	Maximum (per cent.)	Average (per cent.)	Minimum (per cent.)	Maximum (per cent.)
SiO_2	29.8	27.7	32.2	32.0	29.0	36.3
Al_2O_3	19.5	13.6	23.5	15.5	10.1	20.5
FeO	1.9	0.5	3.2	0.5	0.1	1.2
MnO	1.1	0.1	2.0	0.6	0.1	1.8
CaO	43.6	39.6	48.2	44.8	33.3	51.4
MgO	1.4	0.3	4.5	2.6	1.8	4.1
SO_3	0.6	trace	2.3	0.1	trace	0.2
S	1.1	0.4	1.9	1.2	0.7	1.6

An indication of the reactivity of a slag is said to be given by the modulus of reactivity expressed by the ratio $\frac{3(\text{CaO}) + 3(\text{MgO}) + (\text{Al}_2\text{O}_3)}{3(\text{SiO}_2) + (2\text{Al}_2\text{O}_3)}$ wherein the terms in parenthesis are the percentages of the constituents. In Germany a slag is rejected if the modulus is less than unity. Other means of investigating the suitability of a slag is Michelson's method of determining the proportion of non-vitrified grains by dissolving in various solutions, or measuring the mechanical resistance of pastes mixed with a solution of caustic soda.

Michelson's method, which is used in Britain, consists of determining the time taken for crystals of gypsum to appear when, under prescribed conditions, a solution of aluminium sulphate is added to the slag. With very reactive slags this phenomenon may occur in about 2.0 seconds. The solution, which is 2.5 per cent. anhydrous $\text{Al}_2(\text{SO}_4)_3$, is applied to about 0.5 milligramme of slag ground to such a degree that it passes a No. 300 British Standard sieve. The observation of the crystal formation is made by microscope with an enlargement of 400. For the determination of the proportion of non-vitrified grains a few milligrammes of slag, ground to a fineness such that it will pass a No. 170 B.S. sieve but is retained on a No. 300 B.S. sieve, are placed under a microscope giving an enlargement of 200. A drop of bromine is added. The number of grains that are substantially opaque are counted and expressed as a percentage of the total number of grains observed in the field of vision. The granulation of the slag is considered unsatisfactory if the amount of opaque grains exceeds 25 per cent.

For the five British slags, termed A, B, C, D, and E respectively, the modulus of reactivity was calculated from the formula given in the foregoing; these slags were also tested by the Michelson method, and the proportions of non-vitreous grains were determined. In accordance with their moduli of reactivity the slags were placed in the following descending order of suitability: E, D, C, A, B, the moduli being 1.59, 1.33, 1.25, 1.16, and 0.86 respectively. Slag E had 29 per cent. of silica, 10 per cent. (the lowest recorded) of alumina, and 51.4 per cent. (the highest recorded) of lime. The least suitable slag, B, had the greatest amount of silica, and the lowest amounts of alumina and lime.

The order of suitability in accordance with the Michelson test was C, D, E, A, B, the times of the appearance of the gypsum crystals being 105 seconds for slag C and 265 seconds for slag B. Slag C had average amounts of silica, alumina, and lime.

The determination of the proportions of non-vitreous grains gave the order of suitability as C, B, A, E, D, the amount for slag C being 14 per cent. and that for slag D 31 per cent. Slag D contained an average amount of silica and lime and almost the lowest amount of alumina.

There was more or less agreement between the results of the first two methods, that is slags C, D, and E were superior to slags A and B, but less agreement in the third method. When the slags were used for the manufacture of blastfurnace cement the order of superiority was A, C, E, D, B. It is seen that the application of the three criteria did not serve a very useful purpose, as slag A, which was

apparently inferior to the others, gave the best cement. This slag had a silica content below the average, almost the highest alumina content and a lime content above the average. Of the fifteen results of the tests for the suitability of the slags, only three results were correctly forecast.

It seems that the suitability of a slag intended for the manufacture of cement should be judged by the quality of the final product, but such a method has obvious disadvantages. Therefore the author conducted tests involving caustic soda and obtained better results, the order of the British slags being shown thereby to be A, C, E, D, B, which corresponds almost exactly to the results of the tests on the cement.

The method, which has now been standardised, is to grind the slag to a fineness corresponding to a specific surface of 4,200 sq. cm. per gramme. Cubes are made of slag concrete composed of 1 part of slag to 6 parts by weight of graded gravel aggregate and a ratio of water to slag of 0.487. The mixing water is a solution of caustic soda, and mixing is continued for three minutes. The cubes, each face of which has an area of 50 sq. cm., are vibrated for two minutes, and at 24 hours a compression test is made. The strengths obtained for the five British slags varied from 174 kg. per square centimetre for slag A to 108 kg. per square centimetre for slag D, but only 19 kg. per square centimetre for slag B.

A Cement Briquette Suitable for Several Tests.

A REPORT issued by the French Technical Institute of Building and Public Works describes researches made to devise a form of cement briquette which can be easily produced in large quantities under uniform conditions and will serve to determine several properties of the cement without the wide variation in results obtained from the present standard briquette. The tronconical-headed cylindrical specimen was found to be not altogether satisfactory, and research was then concentrated on rectangular specimens. More reliable results showing only a small degree of variation were eventually obtained with a right-angled parallelepipedal briquette 90 mm. long with sides of 3.162 cm., giving a cross-sectional area of 10 sq. cm. These briquettes can be made 24 at a time from the same batch of cement in moulds having a tolerance of only ± 0.01 mm., and can be used for the following tests; density; shrinking (longest dimension); compressive, tensile, bending, and shearing strengths; modulus of elasticity by the supersonic method; resistance to impact; and strength under repeated bending. Tests on cement mortars indicate the high degree of accuracy with this shape of briquette. The foregoing is based on a summary of the report given in "Building Science Abstracts."

Recent British Patents Relating to Cement.

Additions to Cement Clinker.

HYDRAULIC cement clinker is ground with the addition of 0.005 to 0.045 per cent. of a compound of the general formula $\text{HO}-\text{R}-(\text{OR}^1)_n-\text{H}$, where R is an alkylene group which may have at least one hydrogen atom substituted by a group with or without replaceable hydrogen, R^1 is an alkylene group which may have one or more hydrogen atoms substituted by a "solubilizing" group, that is, an amino, aldehyde, or sulphonic acid group, or a group without replaceable hydrogen such as a sulphate or sulphonate group, and n is 1 to 6. The addition is normally made to facilitate grinding and improve concrete and other materials made with the cement; alternatively, the additions may be made to cement after grinding. The alkylene groups may contain one to six carbon atoms and may be straight or branched chain. Compounds mentioned include monoethyl-ether, 2-nitropropyl-ether, and 2-aminopropyl-ether of ethylene glycol, and the monoethyl-ether, and monobutyl-ether of diethylene glycol. Cement-dispersing substances, for example, waste sulphite liquor residue, or naphthalene sulphonic acids; wetting agents, for example, lauryl sodium sulphate; accelerators, such as calcium chloride; pozzolanic and similar materials may also be incorporated in the cement mixture.—No. 561,510 Master Builders Co. (U.S.A.), August 29, 1942.

Hydraulic cement clinker is ground with the addition of 0.005 to 0.045 per cent. of a compound of the general formula $\text{HO}-\text{R}-(\text{OR}^1)_n-\text{OH}$, where R and R^1 are alkylene groups of at least two carbon atoms, and which may be straight or branched chain, and n is 1 to 6, the addition being made to facilitate grinding and improve concrete made with the cement. Compounds specified are diethylene, tri-ethylene, or tetra-ethylene glycol; dipropylene glycol; and ethylene butylene glycol. Cement dispersing substances, for example, waste sulphite liquor residue or naphthalene sulphonic acids; wetting agents, such as lauryl sodium sulphate; accelerators, such as calcium chloride; pozzolanic and similar materials may also be incorporated in the mixture. The glycols may be added to cement after grinding.—No. 561,511, Master Builders Co. (U.S.A.) August 29, 1942.

Hydraulic cement clinker is ground with the addition of 0.005 to 0.045 per cent. of ethylene-glycol or propylene glycol or both glycols to facilitate grinding and improve concrete made with the cement. Cement dispersing substances, for example, waste sulphite liquor residue or naphthalene sulphonic acids; wetting agents, such as lauryl sodium sulphate; accelerators, such as calcium chloride; pozzolanic and similar materials may also be incorporated in the mixture. The glycols may be added to cement after grinding.—No. 561,967. Master Builders Co. (U.S.A.), August 29, 1942.

Hydraulic cement clinker is ground with the addition of about 0.005 to 0.1 per cent. of an aliphatic compound of 4 to 12 carbon atoms with at least one hydroxyl group and at least one hydroxyl, sulphate, sulphonic acid, sulphonate, halogen, nitro, nitroso, or primary amino group, to facilitate grinding and improve

concrete made with the cement; alternatively, the addition may be made to cement after grinding. Compounds mentioned include 2-methyl-2,4 pentanediol, 2-amino- or nitro-2-methyl- or ethyl-propanediol, 1,3-butanediol, 2-nitro- or amino-1-butanol, 2-nitro- or amino-2-methyl-1 propanol, and tris (hydroxymethyl) amino- or nitro-methane. Cement-dispersing substances, such as waste sulphite liquor residue; wetting agents, such as lauryl sodium sulphate; accelerators, such as calcium chloride; pozzolanic and similar materials may also be incorporated in the mixture.—No. 561,997, Master Builders Co. (U.S.A.), August 29, 1942.

Gauging Solutions.

Readily soluble lime components of hydraulic cement are formed into insoluble substances by adding during gauging, chromic anhydride, manganese trioxide, molybdic acid, or neutral water-soluble salts of molybdenum, manganese, vanadium or tungsten, for example, by using 0.2 to 4 per cent. solution as gauging water, to reduce the permeability and to increase the strength of concrete or mortar made therefrom. Smaller quantities of the reagent are requisite for quick-setting cements high in alumina. Larger quantities up to 15 per cent. of chromium anhydride may be used to accelerate setting of Portland cement. Reference is made to Specification No. 244,178.—No. 560,985, C. A. Owens, August 14, 1942.

Vandyke brown and a substance, preferably soda, which counteracts its retarding effect, are dissolved in water to form a gauging solution for cement, concrete, and similar materials. The liquid may also contain a dispersing agent, for example, alcohol or sweet spirits of nitre, and also caustic soda.—No. 560,258. F. C. H. Katon, September 24, 1942.

Wood chips, sawdust, and similar materials are soaked, for example, for two days, in a solution of soda, caustic soda and Vandyke brown, and used with cement or cement and sand for making concrete. The solution may also be used with the gauging water. A dispersing agent, for example sweet spirits of nitre, may be included in the solution.—No. 562,141, F. C. H. Katon, December 14, 1942.

Charts for Control of the Quality of Cement.

In our number for May, 1946, methods of the analysis of the results of tests of Portland cement, particularly routine tests, by quality-control charts are described. The British Standards Institution has now issued B.S. No. 1313 (1947), "Fraction-Defective Charts for Quality Control," in which a method of the control of quality is described, that is the examination of the results of tests to determine the number of defective specimens in each group of specimens. Methods that are easy to use, and which in some cases may replace complete routine examinations, are described and examples are given.

Mechanical Excavation of Clay.

SOME data on the mechanical excavation of clay are given in a recent number of "Claycraft," in which Mr. S. H. Hollowday discusses the use of excavators in clay pits. The capacity of the bucket of the largest excavator operating in clay in Britain is said to be 12 cu. yd. A $\frac{3}{4}$ -cu. yd. bucket is capable of excavating from 10 to 20 cu. yd. of clay per hour, but is only suitable for small works. It is suggested that a walking dragline having a boom of 90 ft. with a $2\frac{1}{4}$ -cu. yd. bucket, and with the weight widely distributed, so that the machine is not easily bogged, may in time become common in this country. A deep-digging dragline is said to be suitable only in a large pit of friable clay; these machines can work a face 80 to 100 ft. high and discharge into wagons on the top of the bank. It is explained that steam is the ideal power for excavating, but the cost is about seven times that of electrical or diesel power.

Mr. J. L. Sturrock describes the use in clay pits of pneumatic-tyred, motor-operated dumpers; ranging in capacity from 1 to 9 cu. yd. They are used for distances up to half a mile on flat ground and are specially suitable for sticky material if a discharge plate is used, but their operation is restricted on wet clayey ground. Their speed is from 10 to 25 miles per hour, and they can operate on slopes of 1 in 4 to 1 in 10, depending on the nature of the surface. It is said that a dumper may have an estimated economical life of about 20,000 hours. The cost of haulage by means of dumpers is about the average of the costs of the various methods of transporting clay.

Reduction of Coal Consumption

THE materials used in France since 1939 to reduce the amount of coal consumed in the manufacture of cement include waste from coal and lignite mines, process clinkers, dusts and slurries from other processes involving combustion, and locomotive ashes. The materials are first treated to remove matter having a low combustible value. According to M. E. Lamaire, writing in "Le Génie Civil," anthracite residues gave the best results of the many materials and methods investigated.

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